

Isotope effects in high- T_c cuprate superconductors: Ultimate proof for bipolaron theory of superconductivity

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Developing a theory of high-temperature superconductivity in copper oxides is one of the outstanding problems in physics. Twenty-five years after its discovery [1], no consensus on the microscopic theory has been reached despite tremendous theoretical and experimental efforts. Attempts to understand this problem are hindered by the subtle interplay among a few mechanisms and the presence of several nearly degenerate and competing phases in these systems. Here we provide unified parameter-free explanation of the observed oxygen-isotope effects on the critical temperature, the magnetic-field penetration depth, and on the normal-state pseudogap for underdoped cuprate superconductors within the framework of the bipolaron theory compatible with the strong Coulomb and Fröhlich interactions, and with many other independent observations in these highly polarizable doped insulators. Remarkably, we also quantitatively explain the measured critical temperature and the magnitude of the magnetic-field penetration depth. The present work thus represents an ultimate proof of the bipolaron theory of high-temperature superconductivity, which takes into account essential Coulomb and electron-phonon interactions.

In 1911 curiosity concerning the electrical properties of metals at low temperatures led the Dutch physicists, Kamerling Onnes and his assistant G. Holst to discover superconductivity at 4.2 K in mercury [2]. This discovery was one of the most important experimental findings in low temperature physics. On the long way towards a microscopic understanding of superconductivity, the observation of an isotope effect on the critical temperature, T_c in 1950 [3, 4] gave an important clue to the microscopic mechanism of superconductivity. The presence of an isotope effect thus implies that superconductivity is not of purely electronic origin. In the same year Fröhlich [5] pointed out that the electron-phonon interaction gave rise to an attractive interaction between electrons, which might be responsible for superconductivity. Fröhlich's theory played a decisive role in establishing the correct mechanism. Finally, in 1957, Bardeen, Cooper and Schrieffer [7] (BCS) developed the BCS theory that was the first successful microscopic theory of superconductivity. The BCS theory implies an isotope-mass dependence of T_c , with an isotope-effect exponent $\alpha = -d \ln T_c / d \ln M = 1/2$, in excellent agreement with the reported isotope exponents in simple metallic superconductors like Hg, Sn and Pb.

The doping dependent oxygen-isotope effect (OIE) on the critical temperature T_c , $\alpha^O = -d \ln T_c / d \ln M_O$ (where M_O is the oxygen-isotope mass)[8] and the substantial OIE on the in-plane supercarrier mass m_{ab}^{**} , $\alpha_{m^*}^O = dm_{ab}^{**} / d \ln M_O$ (ref. [9–14]), provide direct evidence for a significant electron-phonon interaction (EPI) also in high-temperature cuprate superconductors. High resolution angle-resolved photoemission spectroscopy (ARPES) [15] provides further evidence for

the strong EPI apparently with c-axis-polarised optical phonons. These results along with optical [16], neutron scattering [17, 18], and tunneling data [19–21] unambiguously show that lattice vibrations play a significant but unconventional role in high-temperature superconductivity. The interpretation of the optical spectra of high- T_c materials as due to multi-polaron absorption [22] strengthens the view [23] that the Fröhlich EPI is important in those structures. Operating together with a shorter-range deformation potential and molecular-type (e.g., Jahn-Teller [24]) EPIs, the Fröhlich EPI can readily overcome the Coulomb repulsion at a short distance of about the lattice constant for electrons to form real-space intersite bipolarons (see [25] and Supplementary Information [26]).

Despite all these remarkable and well-done experiments that lead to the consistent conclusion about the important role of EPI in high-temperature superconductors, there is no consensus on the microscopic origin of the observed unconventional isotope effects on the in-plane magnetic-field penetration depth and the normal-state pseudogap. The doping dependent α^O has been explained as due to the doping independent oxygen-isotope effect on the in-plane carrier concentration n , that is, $\alpha_n^O = -d \ln n / d \ln M_O = 0.146$ (ref. [27]). This interpretation contradicts other independent experiments [11, 12, 14] which consistently show that the carrier concentrations of the two oxygen-isotope samples are the same within 0.0004 per Cu. This is also in sharp contrast to the observed very large oxygen-isotope effect on the low-temperature magnetic-field penetration depth, $\lambda_{ab} \propto (m_{ab}^{**}/n)^{1/2}$, in both $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$ (ref. [12]) and $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ (ref. [28]), which would lead

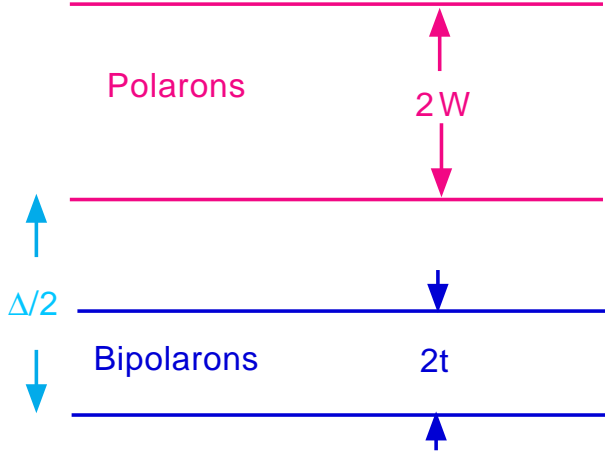


FIG. 1: (Color online) Low energy excitations in cuprate superconductors.

to $\alpha_n^O \simeq 2$ if one would assume that the supercarrier mass is independent of the oxygen mass. Another model based on the pair-breaking effects due to impurities, disorder, and/or pseudogap can also explain the observed oxygen-isotope effects on the penetration depth and the critical temperature in deeply underdoped samples [29]. But this model cannot consistently explain the negligibly small α^O but the large OIE on the penetration depth in optimally doped samples [13].

Alternatively, the bipolaron theory of superconductivity [25] can naturally account for the substantial $\alpha_{m^*}^O$ and large α^O in deeply underdoped cuprates [30]. There is a qualitative difference between ordinary metals and polaronic conductors. The renormalized effective mass of electrons is independent of the ion mass M in ordinary metals (where the Migdal adiabatic approximation is believed to be valid), because the EPI coupling constant λ does not depend on the isotope mass (see, for instance ref. [26]). However, when electrons form polarons (new quasiparticles dressed by lattice distortions), their effective mass m^* depends on M [30].

Although the bipolaron theory can qualitatively explain both $\alpha_{m^*}^O$ and α^O in deeply underdoped samples, some important issues have not been well addressed by the theory. The first issue is why $\alpha_{m^*}^O$ is not equal to α^O even in deeply underdoped cuprates. The second issue is why α^O is much smaller than $\alpha_{m^*}^O$ for slightly underdoped samples. The third issue is why there is a giant negative oxygen-isotope effect on the pseudogap formation temperature T^* in $\text{HoBa}_2\text{Cu}_4\text{O}_8$ (ref. [31]). Here we provide parameter-free explanations to the observed oxygen-isotope effects on the critical temperature, the in-plane supercarrier mass, and on the normal-state pseudogap in $\text{HoBa}_2\text{Cu}_4\text{O}_8$ within the framework of the bipolaron theory. The present work thus represents an ultimate proof of the bipolaron theory of high-temperature superconductivity.

We adopt the bipolaronic low-energy excitation structure of cuprates, Fig. 1, derived from the microscopic Hamiltonian with the strong Coulomb and Fröhlich interactions [25, 26]. The critical temperature of quasi-two-dimensional (2D) bipolarons, which are hard-core bosons, depends on their density $n_b(T_c)$ at the critical temperature and the in-plane bipolaron mass m_{ab}^{**} :

$$T_c \propto \frac{n_b(T_c)}{m_{ab}^{**}}. \quad (1)$$

The bipolaron density slightly depends on temperature due to bipolaron depletion into unbound single polarons, $n_b(T) = [x - n_p(T)]/2$, with the density n_p given by

$$n_p(T) = \frac{k_B T}{W} \ln(1 + e^{-\Delta/2k_B T}), \quad (2)$$

where W is the polaron half-bandwidth, x is the in-plane doping level, and Δ is the bipolaron binding energy, Fig. 1. This expression is obtained by integrating the Fermi-Dirac distribution function with a constant (2D) density of states in the polaron band, $N(E) = 1/2W$ and assuming that the polaron half-bandwidth is large enough, $W \gg k_B T_c$,

$$n_p(T) = \int_0^{2W} dE \frac{2N(E)}{1 + \exp[(\Delta/2 + E)/k_B T]}. \quad (3)$$

Here we take into account that the chemical potential is zero in the superconducting state at and below T_c if all energies are taken with respect to the bipolaron ground state. The polaron in-plane effective mass, $m_{ab}^* \propto \exp(A\sqrt{M})$ (A is a constant), the polaron inverse bandwidth, $1/W$, and the inter-site bipolaron mass m_{ab}^{**} have the same isotope exponent $d \ln m_{ab}^{**} / d \ln M \equiv \alpha_{m^*} = (1/2) \ln(m_{ab}^*/m)$ [30], where m is the band mass in a rigid lattice. The isotope effect on the pseudogap is given by:

$$\delta\Delta = -\frac{3}{2}\delta W = \frac{3W}{2} \frac{\delta m_{ab}^{**}}{m_{ab}^{**}}, \quad (4)$$

and

$$\frac{d \ln \Delta}{d \ln M} = \alpha_{m^*} \frac{3W}{2\Delta}. \quad (5)$$

The above expressions are obtained by taking into account that the pseudogap in Fig. 1 is given by $\Delta/2 = J_p/2 - (W - t/2) = J_p/2 - 3W/4$, where J_p is the phonon-induced intersite attraction, which is *independent* of the ionic mass [26], and $t \approx W/2$ in the intermediate coupling regime [13]. Then using Eqs. (1, 2) and neglecting the terms on the order of $k_B T_c/W \ll 1$, one readily obtains the ratio:

$$\frac{\alpha}{\alpha_{m^*}} = 1 - \frac{1}{[x - n_p(T_c)][1 + \exp(\Delta/2k_B T_c)]}. \quad (6)$$

Eq. 6 can naturally explain why $\alpha_{m^*}^O$ is always larger than α^O [11, 12]. It is worth noting that Eq. 6 is valid

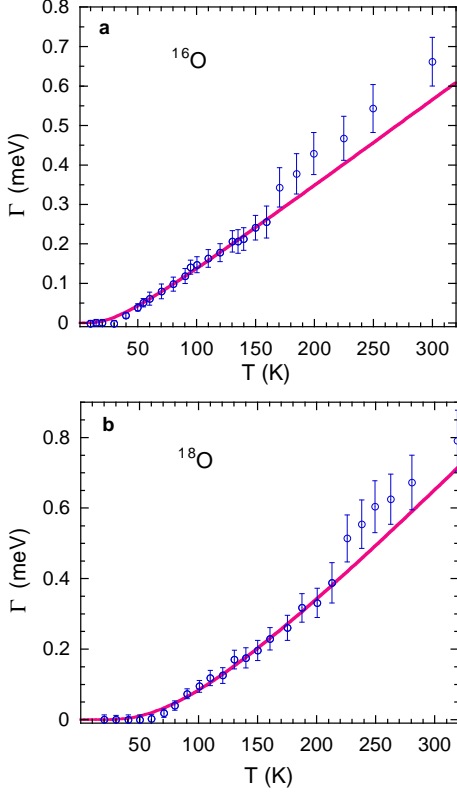


FIG. 2: (Color online) The relaxation rate Γ of crystal-field excitations for the ^{16}O and ^{18}O samples of slightly underdoped $\text{HoBa}_2\text{Cu}_4\text{O}_8$. The data are taken from ref. [31]. The solid red lines represent the best fits of Eq. 8 to the data below T^* . The best fits yield $\Delta/k_B = 94.6 \pm 8.8$ K for the ^{16}O sample and $\Delta/k_B = 286 \pm 19$ K for the ^{18}O sample.

only if $d \ln \Delta / d \ln M$ is small. When $d \ln \Delta / d \ln M$ is large, we need to use Eqs. 1 and 2 to directly calculate the T_c and $n_p(T_c)$ changes upon the isotope exchange, that is,

$$\frac{\delta T_c}{T_c} = -\frac{\delta m_{ab}^{**}}{m_{ab}^{**}} - \frac{\delta n_p(T_c)}{x - n_p(T_c)} \quad (7)$$

Using the above equations we can quantitatively explain the oxygen-isotope effects on the pseudogap and the critical temperature in slightly underdoped $\text{HoBa}_2\text{Cu}_4\text{O}_8$ (ref. [31]). The oxygen isotope effect on the relaxation rate of crystal-field excitations in this compound was investigated by means of inelastic neutron scattering [31]. The relaxation rate, which is related to the free-carrier spin density, clearly shows a large oxygen-isotope effect (see Fig. 2). For the ^{16}O sample there is evidence for the opening of an electronic gap in the normal state at $T^* \simeq 170$ K while for the ^{18}O sample T^* is shifted to about 220 K. In contrast, the T_c is shifted from 79.0 to 78.5 K upon replacing ^{16}O with ^{18}O (the ^{18}O concentration is about 75%) [31].

In a normal state with no pseudogap, the relaxation

rate $\Gamma_n(T)$ is proportional to $[J_{ex}N(E_F)]^2T$, where J_{ex} is the exchange integral between the $4f$ electrons of the Ho^{3+} ions and the charge carriers and $N(E_F)$ is the electronic density of states at the Fermi energy [31]. Within the polaron/bipolaron framework, $N(E_F) = 1/2W \propto m_{ab}^* \propto m_{ab}^{**}$, so the oxygen-isotope effect on $N(E_F)$ is the same as the oxygen isotope effect on m_{ab}^{**} . For a slightly underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ film, $\delta m_{ab}^{**}/m_{ab}^{**}$ was found to be 5.5% upon replacing ^{16}O with ^{18}O (the ^{18}O concentration is about 95%) [14]. If we assume that the oxygen-isotope effect on m_{ab}^{**} for $\text{HoBa}_2\text{Cu}_4\text{O}_8$ is similar to that for the slightly underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ film, we expect that $\delta m_{ab}^{**}/m_{ab}^{**} = 4.3\%$ in $\text{HoBa}_2\text{Cu}_4\text{O}_8$.

In the superconducting state or below T^* , the relaxation rate is suppressed due to opening of the gap. Then the relaxation rate is given by [31]:

$$\Gamma \propto T \exp(-\Delta/2k_B T). \quad (8)$$

The solid lines in Fig. 2 represent the best fits of Eq. 8 to the data below T^* . The best fits yield $\Delta/k_B = 94.6 \pm 8.8$ K for the ^{16}O sample and $\Delta/k_B = 286 \pm 19$ K for the ^{18}O sample. Therefore, there is a giant oxygen-isotope effect on the pseudogap, in agreement with Eq. 4. Substituting $\delta\Delta = 16.5$ meV and $\delta m_{ab}^{**}/m_{ab}^{**} = 4.3\%$ into Eq. 4, we find $W = 0.256$ eV and $t = 0.128$ eV. Using $m_{ab}^{**} = 2\hbar^2/ta^2$, we calculate $m_{ab}^{**} = 8.1 m_e$, which is very close to that ($8.3 m_e$) inferred for the slightly underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.88}$ with $T_c = 87.9$ K (see ref. [33]).

From the Δ , T_c , and W values of the ^{16}O and ^{18}O samples, we can directly calculate $n_p(T_c)$ to be 0.0117 and 0.0038 for the ^{16}O and ^{18}O samples, respectively. Substituting $\delta T_c/T_c = -0.63\%$ and $\delta m_{ab}^{**}/m_{ab}^{**} = 4.3\%$ into Eq. 7, we obtain $\delta n_p(T_c)/[x - n_p(T_c)] = -3.67\%$. With the $n_p(T_c)$ values for the ^{16}O and ^{18}O samples, we find $x = 0.227$. Since the in-plane doping level x in the optimally-doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ was found to be 0.264 (ref. [20]), our inferred doping level of 0.223 for $\text{HoBa}_2\text{Cu}_4\text{O}_8$ is consistent with the fact that this compound is slightly underdoped. With $m_{ab}^{**} = 8.1 m_e$ and $x = 0.227$, we calculate $\lambda_{ab}(0) = 2248$ Å, which is close to $\lambda_a(0) = 2000$ Å for $\text{YBa}_2\text{Cu}_4\text{O}_8$ (ref. [19]).

The exponent $\alpha_{m^*}^O$ of the oxygen-isotope effect on m_{ab}^{**} is calculated to be 0.46 for the slightly underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ and $\text{HoBa}_2\text{Cu}_4\text{O}_8$. Since the exponent $\alpha_{m^*}^{\text{Cu}}$ of the copper-isotope effect on T_c is similar to $\alpha_{m^*}^O$ in the underdoped regime [37, 38], we expect that $\alpha_{m^*}^O \simeq \alpha_{m^*}^{\text{Cu}}$ and $\alpha_{m^*} \simeq 2\alpha_{m^*}^O$. The mass enhancement factor is then equal to $\exp(4\alpha_{m^*}^O) = 6.3$. The bare bandwidth $D = 2W \exp(4\alpha_{m^*}^O) = 3.2$ eV, in quantitative agreement with the band-structure calculations [39].

In the absence of charge localization, as the case of the stoichiometric $\text{HoBa}_2\text{Cu}_4\text{O}_8$, the Bose-Einstein condensation temperature T_c is given by [16]

$$k_B T_c = \frac{2tn_b(T_c)}{1 + \ln(k_B T_c/2t_c)}, \quad (9)$$

where t_c is related to the out-of-plane bipolaron mass m_c^{**} as $t_c = \hbar^2/2m_c^{**}d^2$. The out-of-plane bipolaron mass m_c^{**} is deduced to be $518 m_e$ using $m_c^{**}/m_{ab}^{**} = 64$ at T_c (ref. [36]) and $m_{ab}^{**} = 8.1 m_e$. Then we calculate $t_c = 0.160$ meV. Substituting $t = 0.128$ eV, $t_c = 0.160$ meV, and $n_b(T_c) = 0.1077$ into the above equation, we calculate $T_c = 78.9$ K, in quantitative agreement with the measured T_c (79.0 K). We further show that (see Supplementary Information [26]) Eq. 20 can also quantitatively explain the underdoped $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_4$ with $T_c = 29$ K but overestimates the T_c 's of some optimally doped samples. This implies that optimally doped cuprates are in the crossover regime from bipolaronic real-space pairing to the Cooper pairing of polarons [25].

Apart from the striking isotope effects explained quantitatively here there is abundant independent evidence in favor of bipolarons and the Bose-Einstein condensation in underdoped cuprate superconductors. In particular, the parameter-free estimates of the Fermi energy using the magnetic-field penetration depth [41] and the magnetic quantum oscillations [42] yielded a very low value (below 50 meV) supporting the real-space pairing in underdoped cuprate superconductors. Magnetotransport and thermal magnetotransport data strongly support preformed bosons in cuprates. In particular, many high-magnetic-field studies revealed the non-BCS upward curvature of the upper critical field $H_{c2}(T)$ as a function of temperature [43] as predicted for the Bose-Einstein condensation of charged bosons in the magnetic field [44]. The Lorenz number differs significantly from the conventional Sommerfeld value of the standard Fermi-liquid theory because the carriers are double charged bosons [45]. Direct measurements of the Lorenz number using the thermal Hall effect just above T_c [46] produce its value, which is about the same as that predicted by the bipolaron model. The unusual normal-state diamagnetism uncovered by torque magnetometry has been convincingly explained as the normal state (Landau) diamagnetism of charged bosons [47]. Single polarons, localised within an impurity band-tail, coexist with bipolarons in the charge-transfer doped Mott-Hubbard insulator, where the chemical potential is pinned within the charge-transfer gap due to bipolaron formation. This band-tail model accounts for two energy scales in ARPES and in the extrinsic and intrinsic tunnelling, their temperature and doping dependence, and for the asymmetry and inhomogeneity of extrinsic tunnelling spectra of cuprates [48].

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Supplementary Information—Isotope effects in high- T_c cuprate superconductors: Ultimate proof for bipolaron theory of superconductivity

1 Microscopic derivation of the low-energy band-structure

In highly polarizable ionic lattices like cuprate superconductors both the Coulomb repulsion and the Fröhlich electron-phonon interaction (EPI) are quite strong (of the order of 1 eV) compared with the low Fermi energy of doped carriers because of a poor screening by non- or near-adiabatic carriers [1]. In those conditions the BCS-Eliashberg theory [2] breaks down because of the polaronic collapse of the electron bandwidth [3] so that one has to apply a non-adiabatic small polaron theory [4].

Here we sketch the microscopic derivation of the low-energy band structure, Fig. 1, using the analytical multi-polaron theory in the strong-coupling regime for highly polarizable lattices (more details are found in Refs. [4]).

Quantitative calculations of the interaction matrix elements can be performed from pseudopotentials using the density functional theory (DFT) [5]. On the other hand, one can express the bare Coulomb repulsion and EPI through material parameters rather than computing them from first principles in many physically important cases [6]. In particular, for a polar coupling to longitudinal optical phonons (the Fröhlich EPI), which is the major EPI in polar crystals, both the momentum depen-

dence of the matrix element, $M(\mathbf{q})$, and its magnitude are well known, $|M(\mathbf{q})| = \gamma(q)\hbar\omega_0/\sqrt{2N}$ with a dimensionless $\gamma(q) = \sqrt{4\pi e^2/\kappa\Omega\hbar\omega_0 q^2}$, where Ω is a unit cell volume, N is the number of unit cells in a crystal, ω_0 is the optical phonon frequency, and $\kappa = \epsilon_\infty\epsilon_0/(\epsilon_0 - \epsilon_\infty)$. The high-frequency, ϵ_∞ and the static, ϵ_0 dielectric constants are both measurable in a parent polar insulator.

The dielectric response function of strongly correlated electrons is *a priori* unknown. Hence one has to start with a generic Hamiltonian including *unscreened* Coulomb and Fröhlich interactions operating on the same scale since any ad-hoc assumption on their range and relative magnitude might fail,

$$H = - \sum_{i,j} (T_{ij}\delta_{ss'} + \mu\delta_{ij})c_i^\dagger c_j + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{\epsilon_\infty |\mathbf{m} - \mathbf{n}|} \hat{n}_i \hat{n}_j + \sum_{\mathbf{q},i} \hbar\omega_0 \hat{n}_i [u(\mathbf{m}, \mathbf{q})d_{\mathbf{q}} + H.c.] + H_{ph}. \quad (10)$$

Here $T_{ij} \equiv T(\mathbf{m} - \mathbf{n})$ is the bare hopping integral, μ is the chemical potential, $i = \mathbf{m}, s$ and $j = \mathbf{n}, s'$ include both site (\mathbf{m}, \mathbf{n}) and spin (s, s') states, $u(\mathbf{m}, \mathbf{q}) = (2N)^{-1/2}\gamma(q)\exp(i\mathbf{q} \cdot \mathbf{m})$, $c_i, d_{\mathbf{q}}$ are electron and phonon operators, respectively, $\hat{n}_i = c_i^\dagger c_i$ is a site occupation operator, and $H_{ph} = \sum_{\mathbf{q}} \hbar\omega_0 (d_{\mathbf{q}}^\dagger d_{\mathbf{q}} + 1/2)$ is the polar vibration energy.

In highly polarisable lattices with $\epsilon_0 \rightarrow \infty$ the familiar Lang-Firsov (LF) [7] canonical transformation e^S is particularly instrumental with $S = -\sum_{\mathbf{q},i} \hat{n}_i [u(\mathbf{m}, \mathbf{q})d_{\mathbf{q}} - H.c.]$. It shifts the ions to new equilibrium positions changing the phonon vacuum, and removes most of *both* interactions from the transformed Hamiltonian, $\tilde{H} = e^S H e^{-S}$,

$$\tilde{H} = - \sum_{i,j} (\hat{\sigma}_{ij}\delta_{ss'} + \tilde{\mu}\delta_{ij})c_i^\dagger c_j + H_{ph}, \quad (11)$$

where $\hat{\sigma}_{ij} = T(\mathbf{m} - \mathbf{n})\hat{X}_i^\dagger \hat{X}_j$ is the renormalised hopping integral involving the multi-phonon transitions described with $\hat{X}_i = \exp\left[\sum_{\mathbf{q}} u(\mathbf{m}, \mathbf{q})d_{\mathbf{q}} - H.c.\right]$, and $\tilde{\mu} = \mu + E_p$ is the chemical potential shifted by the polaron level shift,

$$E_p = \frac{2\pi e^2}{\kappa} \int_{BZ} \frac{d^3 q}{(2\pi)^3 q^2}. \quad (12)$$

Here, the integration goes over the Brillouin zone (BZ) and $E_p = 0.647$ eV in La_2CuO_4 [1]. The electron-phonon coupling constant is defined as $\lambda = 2E_p N(0)$. In the case of 2D carriers with a constant bare density of states, $N(0) = ma^2/2\pi\hbar^2$ per spin, Eq.(12) places cuprates in the intermediate to strong-coupling regime, $\lambda \gtrsim 0.5$, if the bare band mass $m > m_e$ (here a is the in-plane lattice constant).

The number of virtual phonons in the polaron cloud is large in oxides and some other polar lattices, $E_p/\hbar\omega_0 > 1$ with the characteristic (oxygen) optical phonon frequency $\hbar\omega_0 \lesssim 80$ meV, so that multi-phonon vertexes

are essential in the expansion of the hopping operator $\hat{\sigma}_{ij}$. To deal with this challenging problem let us single out the coherent hopping in Eq.(11) averaging $\hat{\sigma}_{ij}$ with respect to the phonon vacuum, and consider the remaining terms as perturbation, $\tilde{H} = H_0 + H_{p-ph}$. Here

$$H_0 = - \sum_{i,j} (t_{ij}\delta_{ss'} + \tilde{\mu}\delta_{ij})c_i^\dagger c_j + H_{ph} \quad (13)$$

describes free phonons and polarons coherently propagating in a narrow band with the exponentially diminished hopping integral, $t_{ij} = T(\mathbf{m} - \mathbf{n})\exp[-g^2(\mathbf{m} - \mathbf{n})]$,

$$g^2(\mathbf{m}) = \frac{1}{2N} \sum_{\mathbf{q}} \gamma(q)^2 [1 - \cos(\mathbf{q} \cdot \mathbf{m})], \quad (14)$$

and

$$H_{p-ph} = \sum_{i,j} (t_{ij} - \hat{\sigma}_{ij})\delta_{ss'}c_i^\dagger c_j \quad (15)$$

is the residual polaron-multiphonon interaction, which is a perturbation at large λ . In the diagrammatic technique the corresponding vertexes have any number of phonon lines. The second-order in H_{p-ph} polaron self-energy ($\Sigma_p \approx -E_p/2z\lambda^2$) and the phonon self-energy ($\Sigma_{ph} \approx -x\hbar\omega_0/z\lambda^2$) are small, if $\lambda \gg 1/\sqrt{2z}$ [8] (here z is the lattice coordination number and x is the atomic density of carriers). Hence the perturbation expansion in $1/\lambda$ is applied. Importantly there is no structural instability in the strong coupling regime since $|\Sigma_{ph}| \ll \hbar\omega_0$ [8].

The LF transformation, Eq. (11) is exact for any adiabatic ratio $\hbar\omega_0/T(a)$. However, if the perturbation expansion in $1/\lambda$ is restricted by lowest orders, then it significantly overestimates polaron masses in the adiabatic regime, $\hbar\omega_0/T(a) < 1$, for the case of the short-range (Holstein) EPI (here $T(a)$ is the nearest-neighbor bare hopping integral). The polaronic band narrowing factor, $\exp(-g^2)$ becomes very small for this EPI in the strong-coupling regime, which would eliminate any possibility of high temperature superconductivity and even metallicity of the small Hosltein polarons.

However in the case of the long-range (Fröhlich) EPI, Quantum Monte-Carlo simulations [9] show that the LF transformation provides numerically accurate polaron masses already in the zero order of the inverse-coupling expansion both in the adiabatic regime as well as in the non-adiabatic one for *any* strength of the Fröhlich EPI. Moreover, such small polarons [9] and small bipolarons [10] are perfectly mobile in the relevant range of the coupling and the adiabatic ratio.

The perturbation H_{p-ph} has no diagonal matrix elements with respect to phonon occupation numbers. Hence it can be removed from the Hamiltonian in the first order using a second canonical transformation $\mathcal{H} = e^{S_2} \tilde{H} e^{-S_2}$ with $(S_2)_{n'n} = \sum_{i,j} \langle n' | (\hat{\sigma}_{ij} - t_{ij})c_i^\dagger c_j | n \rangle / (E_{n'} - E_n)$, where $E_n, E_{n'}$ and $|n\rangle, |n'\rangle$ are

the energy levels and the eigenstates of H_0 , respectively. Taking into account that the polaron Fermi energy is small compared with the phonon energy at strong coupling and/or sufficiently low doping [1], one can neglect the polaron contribution to $E_{n'} - E_n \approx \hbar\omega_0 \sum_{\mathbf{q}} n'_{\mathbf{q}}$ and project the second-order in $1/\lambda$ Hamiltonian \mathcal{H} onto the phonon vacuum $|0\rangle$ with the following result

$$\mathcal{H} = - \sum_{i,j} (t_{ij} \delta_{ss'} + \tilde{\mu} \delta_{ij}) c_i^\dagger c_j - \sum_{\mathbf{m}\mathbf{n}\mathbf{m}'\mathbf{n}', ss'} V_{\mathbf{m}\mathbf{n}}^{\mathbf{m}'\mathbf{n}'} c_{\mathbf{m}\mathbf{s}}^\dagger c_{\mathbf{n}\mathbf{s}} c_{\mathbf{m}'\mathbf{s}'}^\dagger c_{\mathbf{n}'\mathbf{s}'}, \quad (16)$$

where

$$V_{\mathbf{m}\mathbf{n}}^{\mathbf{m}'\mathbf{n}'} = iT_{ij}T_{i'j'} \int_0^\infty dt e^{-\delta t} \langle 0 | [\hat{X}_i^\dagger(t) \hat{X}_j(t) - 1] \hat{X}_{i'}^\dagger \hat{X}_{j'} | 0 \rangle, \quad (17)$$

and $\hat{X}_i^\dagger(t)$ is the Heisenberg multi-phonon operator obtained by replacing d_q in \hat{X}_i^\dagger with $d_q \exp(i\omega_0 t)$. Calculating the integral, Eq.(17) with $\delta \rightarrow +0$ yields

$$V_{\mathbf{m}\mathbf{n}}^{\mathbf{m}'\mathbf{n}'} = \frac{t_{ij}t_{i'j'}}{\hbar\omega_0} \sum_{k=1}^\infty \frac{f(\mathbf{m}\mathbf{n}, \mathbf{m}'\mathbf{n}')^k}{k!k}, \quad (18)$$

where $f(\mathbf{m}\mathbf{n}, \mathbf{m}'\mathbf{n}') = (1/2N) \sum_{\mathbf{q}} \gamma(q)^2 [\cos(\mathbf{q} \cdot (\mathbf{m} - \mathbf{n}')) + \cos(\mathbf{q} \cdot (\mathbf{n} - \mathbf{m}')) - \cos(\mathbf{q} \cdot (\mathbf{m} - \mathbf{m}')) - \cos(\mathbf{q} \cdot (\mathbf{n} - \mathbf{n}'))]$.

All matrix elements, Eq. (18), of the polaron-polaron interaction are small compared with the polaron kinetic energy except the *exchange* interaction, $J_p(\mathbf{m} - \mathbf{n}) \equiv V_{\mathbf{m}\mathbf{n}}^{\mathbf{m}\mathbf{n}}$ such that $f(\mathbf{m}\mathbf{n}, \mathbf{m}'\mathbf{n}') = 2g^2(\mathbf{m} - \mathbf{n})$. Using $\sum_{k=1}^\infty y^k/k!k = -C - \ln(y) + Ei^*(y)$ with $C \approx 0.577$ and $Ei^*(y) \approx e^y/y$ (for large y) one obtains a substantial $J_p(\mathbf{m}) = T^2(\mathbf{m})/2g^2(\mathbf{m})\hbar\omega_0$, which is larger than the nearest-neighbour polaron hopping integral, $t(a)/J_p \propto 2\hbar\omega_0 g^2 e^{-g^2}/T(a) < 1$. Keeping only this exchange we finally arrive with the polaronic "t- J_p " Hamiltonian [4],

$$\mathcal{H} = - \sum_{i,j} (t_{ij} \delta_{ss'} + \tilde{\mu} \delta_{ij}) c_i^\dagger c_j + 2 \sum_{\mathbf{m} \neq \mathbf{n}} J_p(\mathbf{m} - \mathbf{n}) \left(\vec{S}_{\mathbf{m}} \cdot \vec{S}_{\mathbf{n}} + \frac{1}{4} \hat{n}_{\mathbf{m}} \hat{n}_{\mathbf{n}} \right), \quad (19)$$

where $\vec{S}_{\mathbf{m}} = (1/2) \sum_{s,s'} c_{\mathbf{m}s}^\dagger \vec{\tau}_{ss'} c_{\mathbf{m}s'}$ is the spin 1/2 operator ($\vec{\tau}$ are the Pauli matrices), $\hat{n}_{\mathbf{m}} = \sum_s \hat{n}_{\mathbf{m}s}$, and $\tilde{\mu} = \tilde{\mu} + \sum_{\mathbf{m}} J_p(\mathbf{m})$ is the chemical potential further renormalized by H_{p-ph} .

There is a striking difference between this polaronic t- J_p Hamiltonian and the familiar t-J model derived from the repulsive Hubbard U Hamiltonian in the limit $U \gg t$ omitting the so-called three-site hoppings and EPI [11]. The latter model acts in a projected Hilbert space constrained to no double occupancy. On the contrary in the polaronic t- J_p Hamiltonian, Eq. (19) there is no constraint on the double on-site occupancy since the Coulomb repulsion is negated by the Fröhlich EPI. The polaronic hopping integral $t(a)$ leads to the coherent (bi)polaron band and the antiferromagnetic exchange

of purely phononic origin J_p bounds polarons into small superlight inter-site bipolarons. Last but not least the difference is in the "+" sign in the last term of Eq. (19) proportional to $\hat{n}_{\mathbf{m}} \hat{n}_{\mathbf{n}}$, which protects the ground superconducting state from the bipolaron clustering, in contrast with the "-" sign in the similar term of the standard t-J model, where the phase separation is expected at sufficiently large J [12].

The polaronic t- J_p Hamiltonian, Eq. (19) is analytically solvable in the limit of sufficiently low atomic density of carriers [4]. Neglecting the first term in \mathcal{H} , which is the polaron kinetic energy proportional to $t(a) < J_p$, one can readily diagonalise the remaining spin-exchange part of the Hamiltonian. Its ground state is an ensemble of inter-site singlet bipolarons with the binding energy $\Delta_b = J_p$ localised on nearest neighbor sites. Such small bipolarons repel each other and single polarons via a short-range repulsion of about J_p .

The kinetic energy operator in Eq. (19) connects singlet configurations in the first and higher orders with respect to the polaronic hopping integrals. Taking into account only the lowest-energy degenerate singlet configurations and discarding all other configurations one can project the t- J_p Hamiltonian onto the inter-site bipolaronic Hamiltonian using the bipolaron annihilation operators $B_{\mathbf{m}} = 2^{-1/2}(c_{\mathbf{m}\uparrow} c_{\mathbf{m}+\mathbf{a}\downarrow} - c_{\mathbf{m}\downarrow} c_{\mathbf{m}+\mathbf{a}\uparrow})$, where \mathbf{a} connects nearest neighbors [10]. Such inter-site bipolarons are perfectly mobile since they tunnel via single-polaron transitions [10, 13]. At finite temperatures single polarons, thermally excited above the pseudogap, coexists with these bipolarons as shown in Fig. 1 of the main text.

Small bipolarons are hard-core bosons with the short-range repulsion and a huge anisotropy of their effective mass since their inter-plane hopping is possible only in the second order of the polaron hopping integral [14]. The occurrence of superconductivity in bipolaronic systems is not controlled by the pairing strength, but by the phase coherence among the electron pairs below the Bose-Einstein condensation temperature [15].

2 Parameter-free calculations of the Bose-Einstein condensation temperatures of some cuprate superconductors

In the absence of charge localization, the Bose-Einstein condensation temperature T_c is given by [16]

$$k_B T_c = \frac{2tn_b(T_c)}{1 + \ln(k_B T_c / 2t_c)}, \quad (20)$$

where t is the bipolaron half-bandwidth and t_c is related to the out-of-plane bipolaron mass m_c^{**} as $t_c = \hbar^2 / 2m_c^{**} d^2$ (d is the inter-plane distance). The above equation can be written in terms of the measurable parameters such as the inplane penetration depth and the supercarrier mass anisotropy constant $\gamma^2 = m_c^{**} / m_{ab}^{**}$,

$$k_B T_c = \frac{dh^2 c^2}{16\pi^3 e^2 \lambda_{ab}^2(0)} \times$$

$$[1 + \ln(\frac{32\pi^3 x e^2 k_B T_c \lambda_{ab}^2(0) \gamma^2 d}{a^2 \hbar^2 c^2})]^{-1}. \quad (21)$$

It is worth noting that the T_c value calculated from Eq. 21 should be slightly overestimated due to the fact that $n_b(T_c)$ is slightly lower than $n_b(0) = x/2$. For $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_{4+y}$, $\lambda_{ab}(0) = 291$ nm (ref. [17]), $\gamma = 43$ (ref. [18]), and $x = 0.1$. These parameters lead to $T_c = 31.8$ K, in quantitative agreement with the measured value of 29 K. For the optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ with $T_c = 93$ K, $\lambda_{ab}(0) = 1600$ Å (ref. [19]), $x = 0.264$ (ref. [20]), and $\gamma = 8$ (ref. [21]), so T_c is calculated to be 162 K, which is higher than the measured value of 93 K pointing to the BEC-BCS crossover [3].

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